

Materials Benchmarking Activities For CAMP Facility

Wenquan Lu (PI)

Q. Wu, S. B. Ha, S. Trask, B. Polzin, J. Prakash, D. Dees,
and A. Jansen

Electrochemical Energy Storage
Chemical Sciences and Engineering Division
Argonne National Laboratory

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Vehicle Technologies Program



Overview

Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2017

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE/USABC goals
 - Cost, and
 - Performance.
- High energy active material Identification and evaluation

Budget

- Total project funding in FY2014: \$350K (as part of CAMP effort)
- 100% DOE

Partners and Collaborators

- The Cell Assembly, Modeling, and Prototyping (CAMP) Facility (Andrew Jansen, ANL)
- Materials Engineering Research Facility (MERF) (Gregory Krumdick, ANL)
- Post Test Analysis Facility (Ira Bloom, ANL)
- Prof. Prakash's group (IIT)
- Industries, Research institutes, and Universities



Relevance

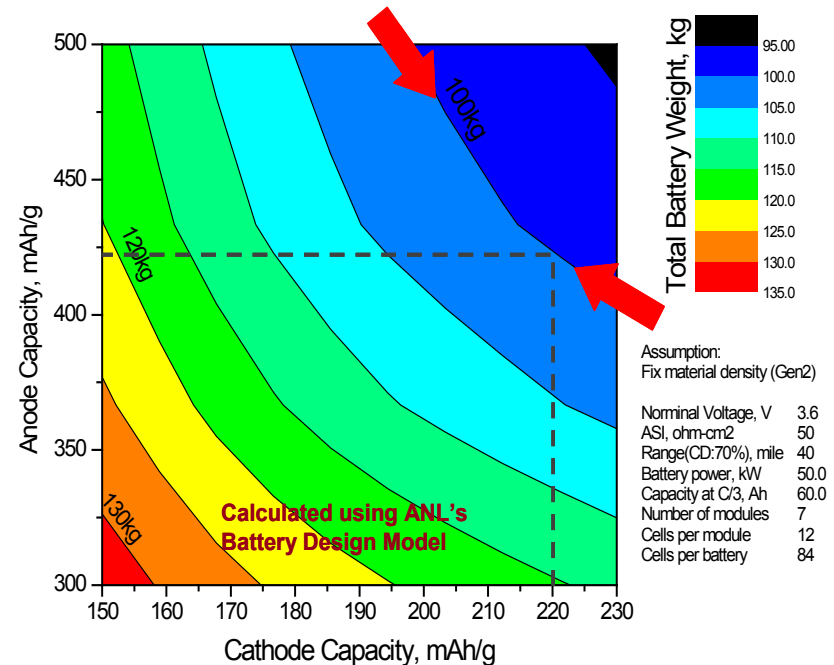
- On one hand, there is no commercially available high energy material to meet the 40 mile PHEV application established by the USABC. On the other hand, an overwhelming number of materials are being marketed/reported by vendors/inventors for Lithium-ion batteries.
- To overcome the “valley of death”, which happens when a new discovery is traversed to commercial product, CAMP Facility can provide a realistic and consistent evaluation of candidate chemistries in a time-effective manner with practical quantities of novel materials.
- However, the CAMP facility is more than an arrangement of equipment, it is an integrated team effort designed to support the production of prototype electrodes and cells. In order to utilize the facility more efficiently and economically, the cell chemistries will be validated internally to determine if they warrant further consideration.
- The benchmarking activities will not only benefit the CAMP facility, but also provide an objective opinion to the material developer. Moreover, the better understanding of the active materials at cell system level will support the material development efforts.



Objectives

- To **identify and evaluate** low-cost cell chemistries that can simultaneously meet the life, performance, abuse tolerance, and cost goals for Plug-in HEV application. **High energy** active materials for both anode and cathode are focus of this project.
- To **enhance the understanding** of advanced cell components on the electrochemical performance and safety of LIB.
- To support the CAMP facility for **prototyping** cell and **electrode library** development, also the MERF facility for **material scale up**, respectively.

Material Requirements for PHEV40



Approach and Strategy

- To collaborate with material developers and leverage ANL's expertise in electrode design and cell testing. High energy silicon anode materials will be validated, mainly in terms of its
 - Electrochemical performance,
 - Electrode optimization, and
 - Thermal stability.
- High energy cathode materials, nickel rich lithium metal oxide, will be investigated.
- The electrochemical performance will be validated using coin type cells. The information will be used to aid large format cell prototyping and testing in the CAMP facility.

USABC Requirements of Energy Storage Systems for PHEV

USABC Requirements of Energy Storage Systems for PHEV

Characteristics at EOL	Unit	PHEV-20 mile	PHEV-40 mile
Reference Equivalent Electric Range	miles	20	40
Peak Discharge Pulse Power (10 sec)	kW	37	38
Peak Regen Pulse Power (10 sec)	kW	25	25
Available Energy for CD (Charge-Depleting) Mode	kWh	5.8	11.6
Available Energy for CS (Charge-Sustaining) Mode	kWh	0.3	0.3
Maximum System Weight	kg	70	120
Maximum System Volume	L	47	80

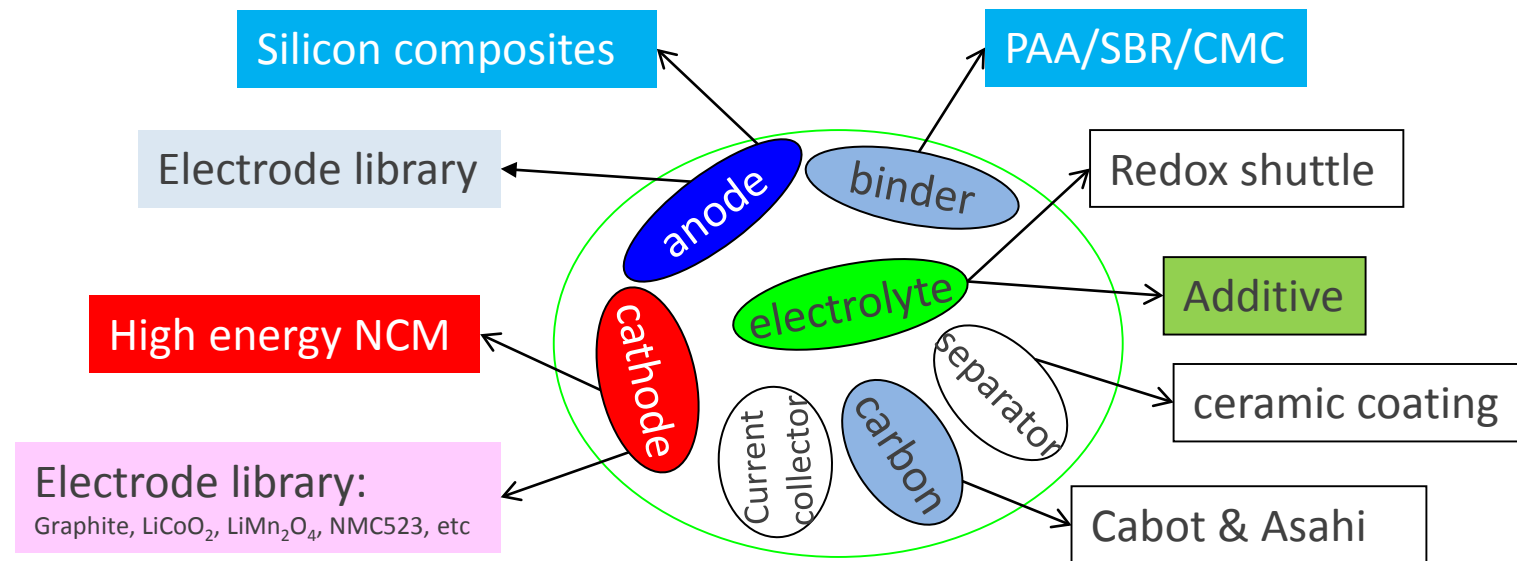
Test Protocol development

- In order to conduct the electrochemical characterization of the battery chemistries for advanced battery research (ABR) program, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.



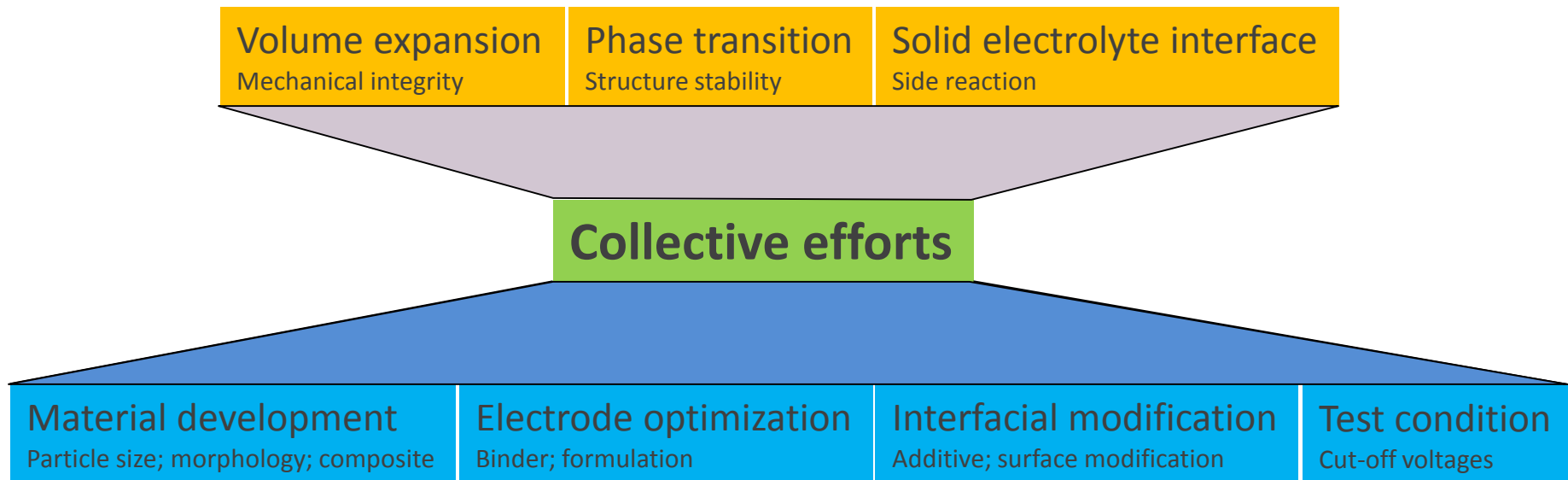
Technical Accomplishments and Milestones

- Several silicon and its composite materials have been identified. The material validation work on silicon and its composite is incorporated with binder investigations. Pouch cells were fabricated and tested at CAMP using the recommended Si.
- High energy cathode materials were investigated in two approaches: increasing cut-off voltage and increase active material fraction in formulation.
- Other cell components, such as electrolyte and additives, conductive additive, separators, binders, etc., have also been investigated.



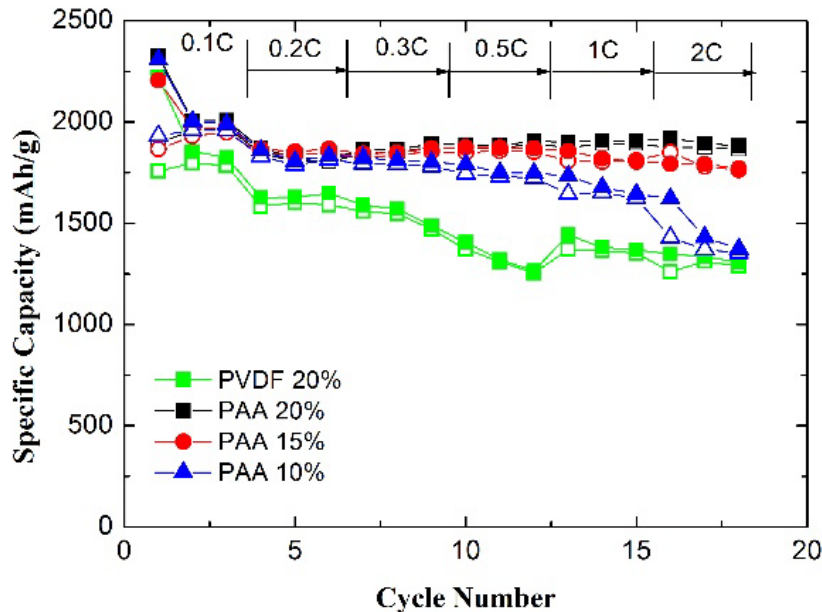
Silicon electrode development

- In addition to material development, a viable silicon electrode for LIB needs collective efforts, including additive, binder, test protocol, electrode engineering.
- The additive and binder's impact on electrochemical and thermal properties was systematically investigated and presented.



Si-G electrode optimization

PAA composition effect on E-Chem

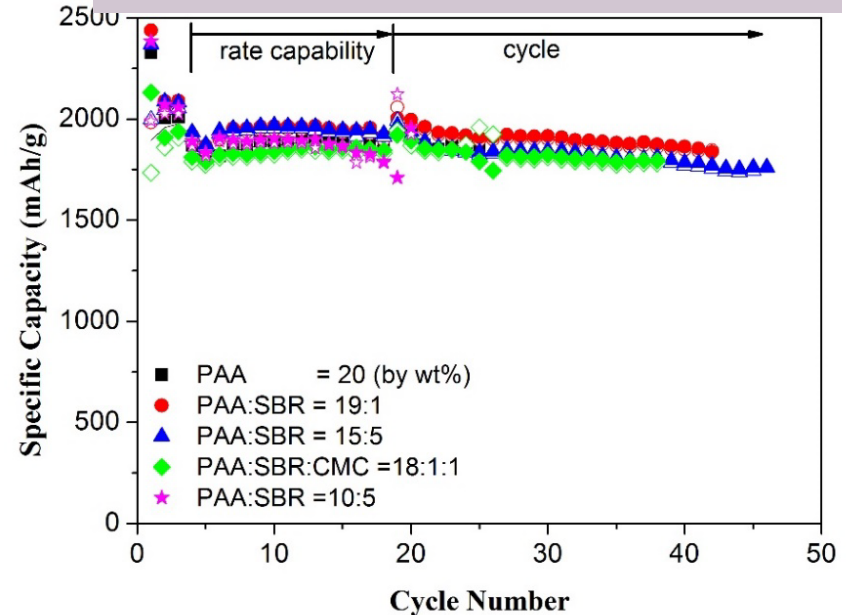


- Si-G* electrode with 20wt.% PAA shows best electrochemical performance, when PAA only binder is used for Si electrode.
- SBR addition to PAA binder can improve the mechanical integrity of Si electrode.

SBR effect on Si-G electrode adhesion



Cycle performance of Si-G electrode

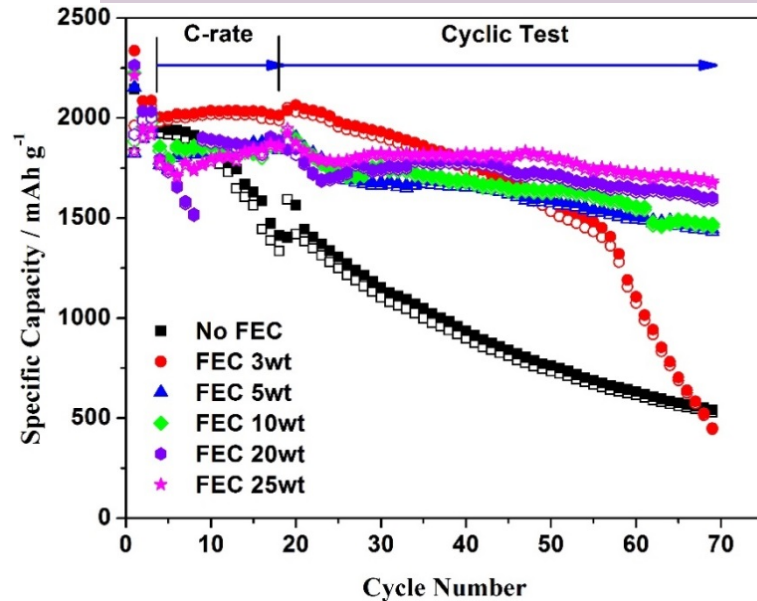


* Si-G: silicon graphene

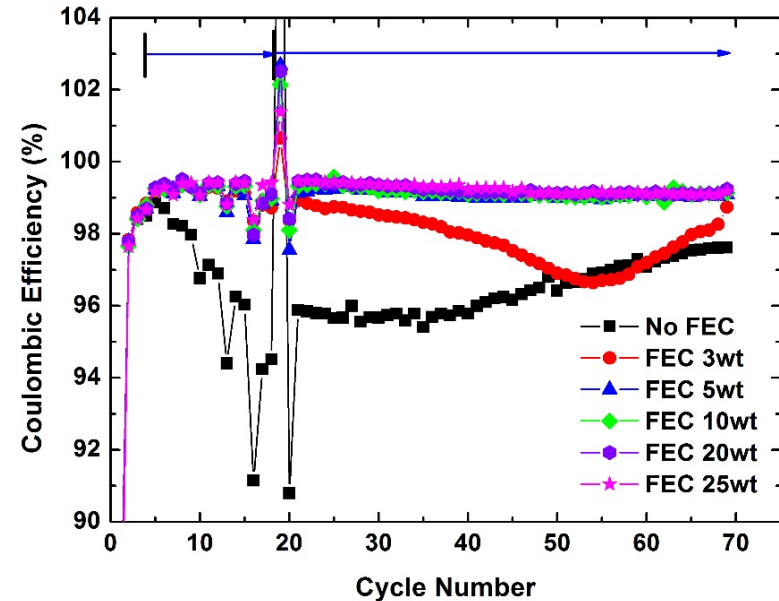
FEC effect on Si-G electrode

- Electrochemical performance

Cycle performance of Li/Si-G cell



Coulombic efficiency of Li/Si-G cell

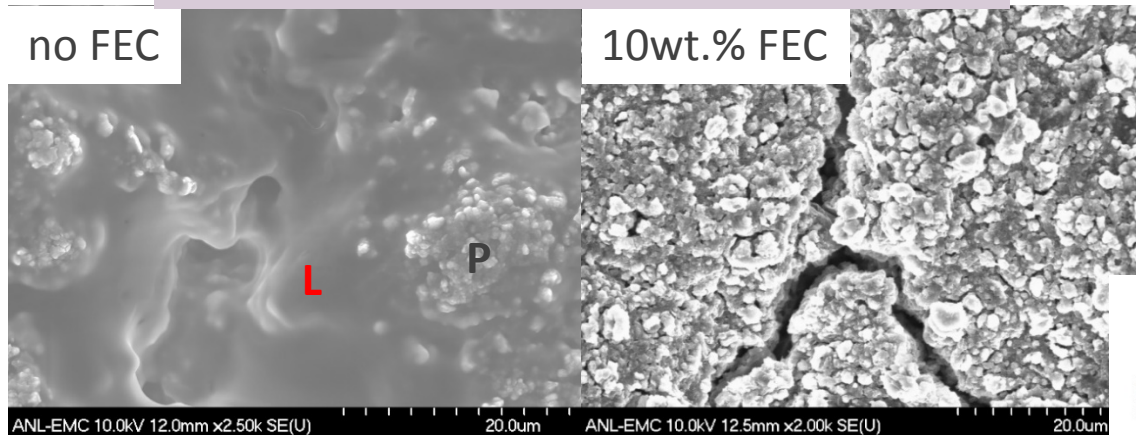


- FEC as an effective additive for Si-G electrode was systematically investigated.
- The minimum FEC content in electrolyte was determined to be over 5wt.% from both cycle performance and coulombic efficiency.

FEC effect on Si-G electrode

- Solid Electrolyte Interface

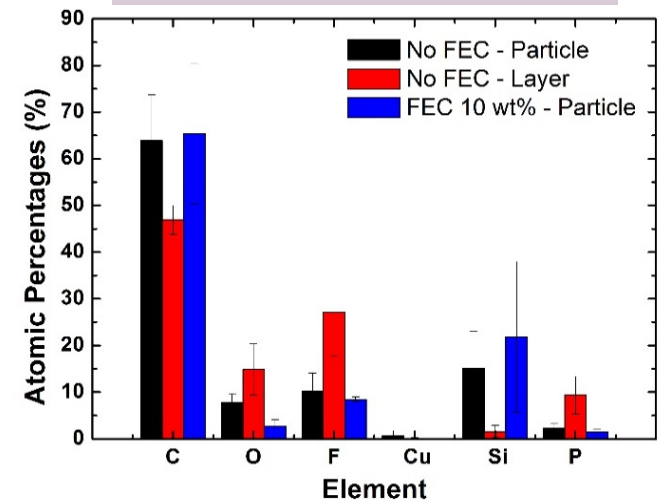
Electrode surface after 3 formation cycles



- SEI film formed on Si-G electrode in FEC free electrolyte probably consists of mainly lithium salt: Li_2CO_3 , ROCO_2Li , et. al., which doesn't prevent the further SEI formation in the following cycles.
- SEI film formed on Si-G electrode in FEC containing electrolyte consists of mainly polycarbonate, which is thin and robust, prevent further electrolyte decomposition.

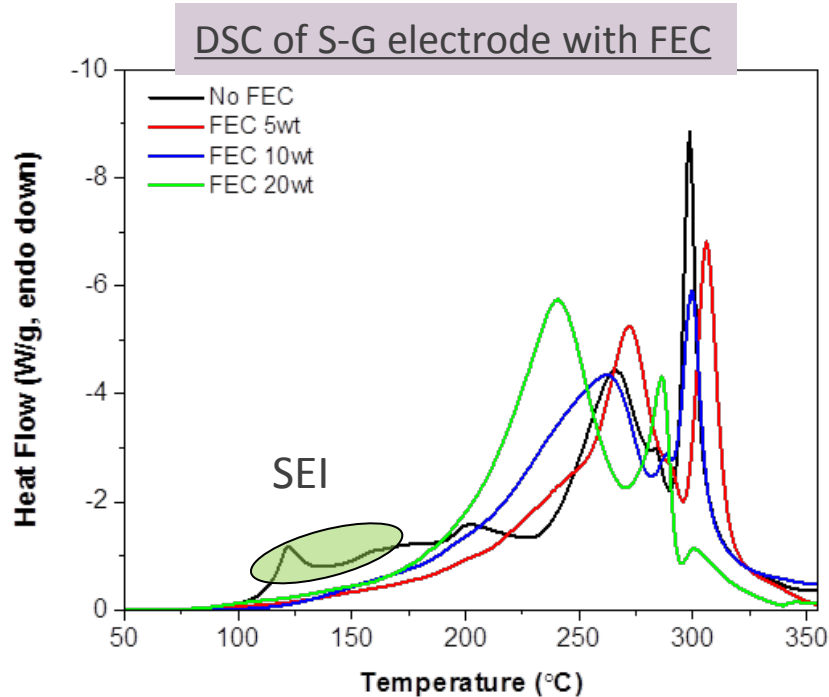
Si-G/PAA (80%/20%)
1.2M LiPF₆ in EC/EMC (3/7)
Formation:
1.5V to 10mV
cha/disch: C/10

EDX results on Si electrode



More Si, but less O, P, and F observed on the electrode in FEC containing electrolyte.

Thermal stability of Si-G electrode

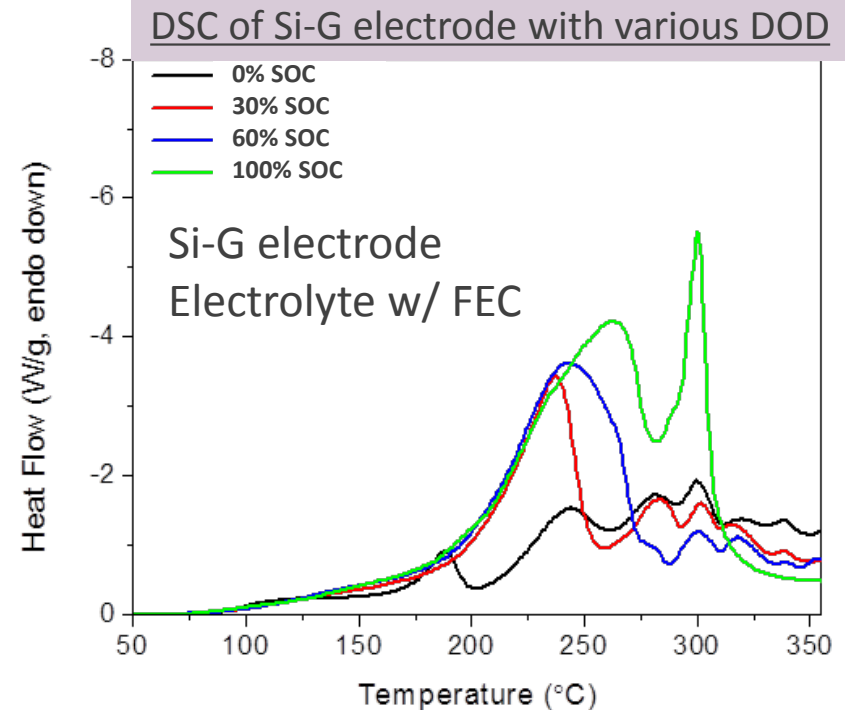


FEC effect

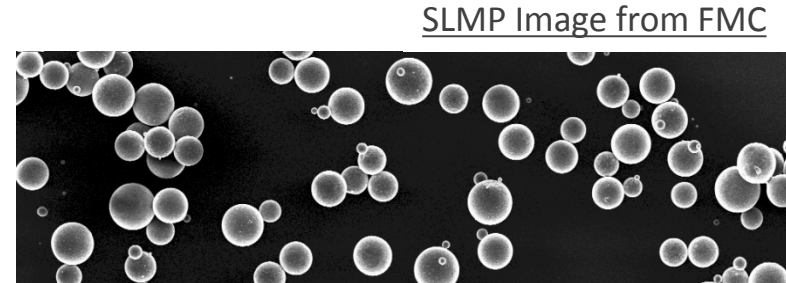
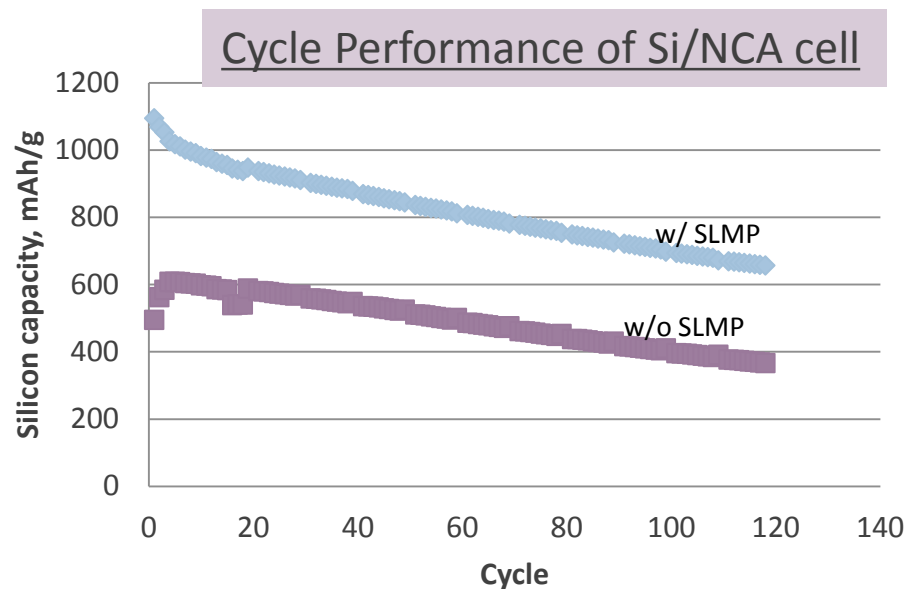
- The solid electrolyte interface (SEI) is different when FEC is used as additive
- SEI amount is less with FEC containing electrolyte is used, resulting into less heat generation.

State of Charge effect

- The highly lithiated Si shows more exothermal reaction above 220°C.
- However, the exothermic reaction related to SEI decomposition below 200°C is almost same.

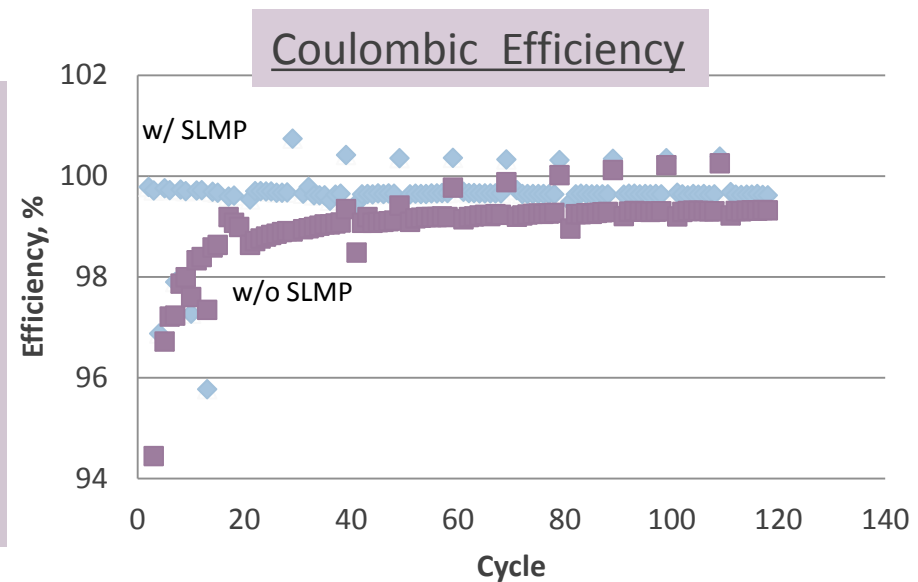


Prelithiation effect on Si-G/NCA* cell



Si-G/NCA cell (N/P=1.6)
1.2M LiPF₆ in EC/EMC w/ SLMP
Si-G prepared @ANL
Prelithiation by FMC

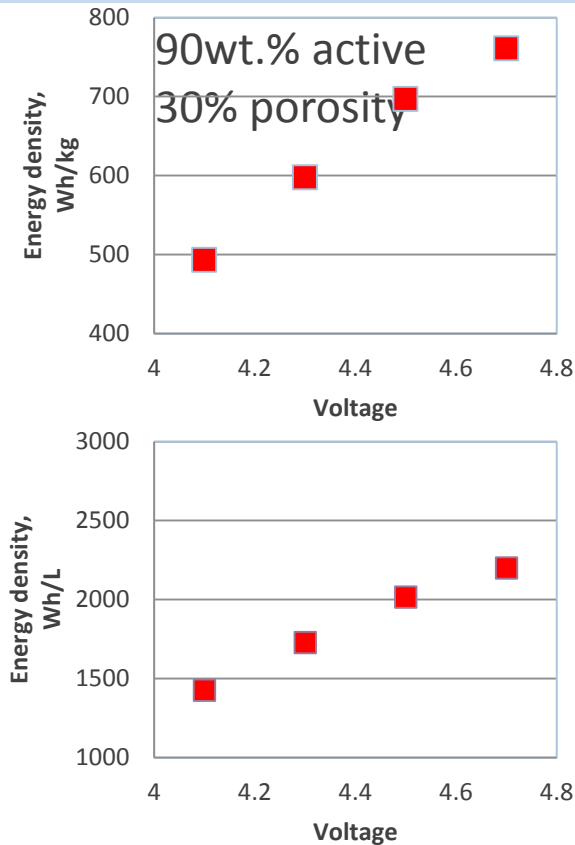
- Prelithiation apparently can mitigate the irreversible capacity loss during 1st cycle.
- During the cycling test, the coulombic efficiency is constantly high for the prelithiated Si-G/NCA cell.
- However, little impact on capacity fading is observed.



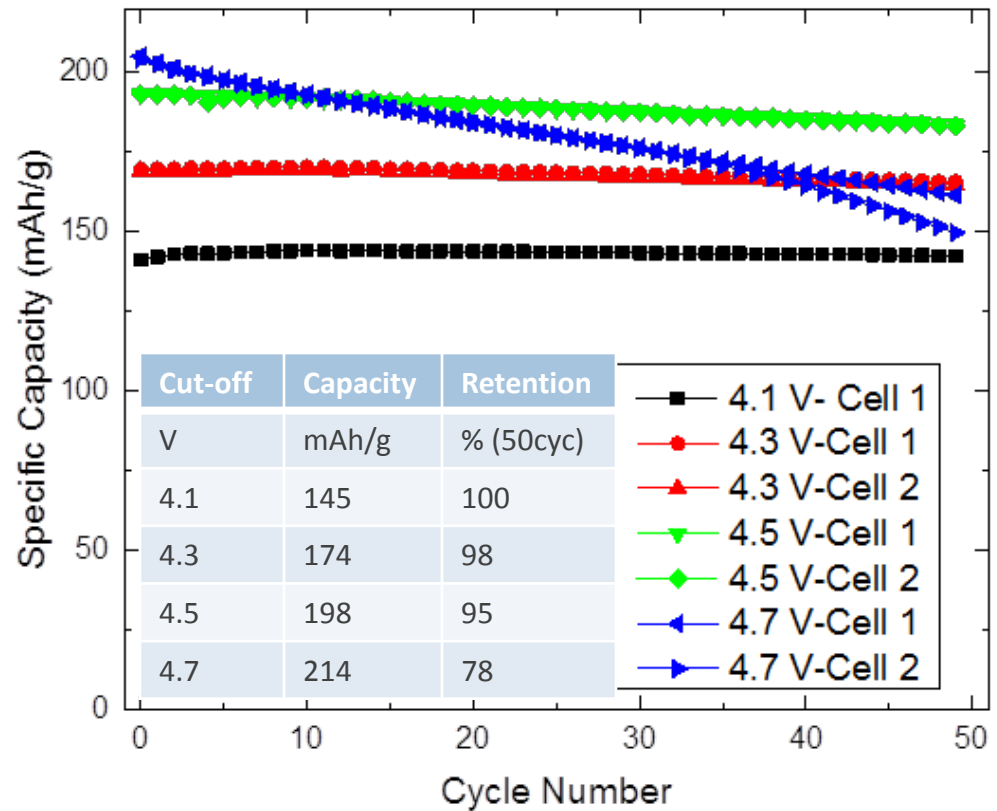
* NCA: LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (Toda)

High energy cathode: $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523)

Energy density* vs. cut-off voltage



Cycle performance of NCM with various cut-off voltage



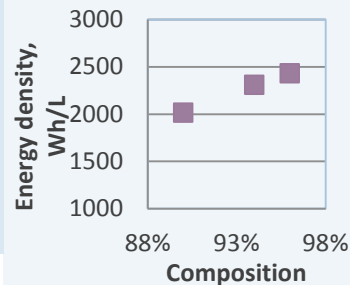
- High nickel content cathode NCM523 (Toda) can provide 50% more both gravimetric and volumetric energy density when 4.7V was used as cut-off voltage.
- In Li/NCM523 half cell, good capacity retention was obtained up to 4.5V.

* Energy density was calculated according to total coating materials, including additive and binder.

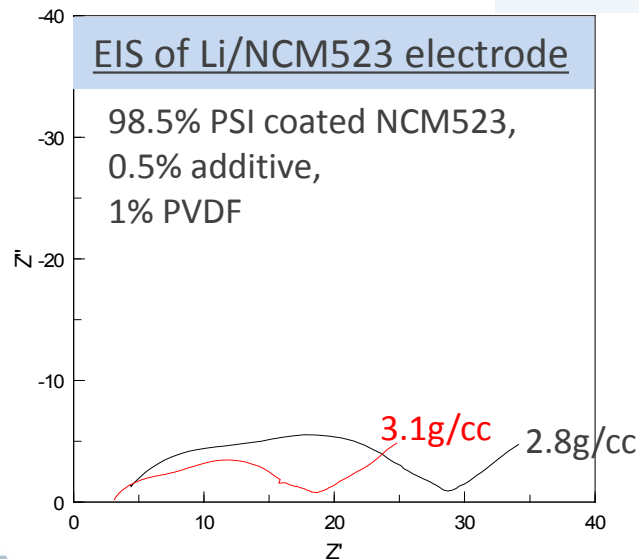
Engineering to high energy electrode

- PSI electrode calendered at ANL

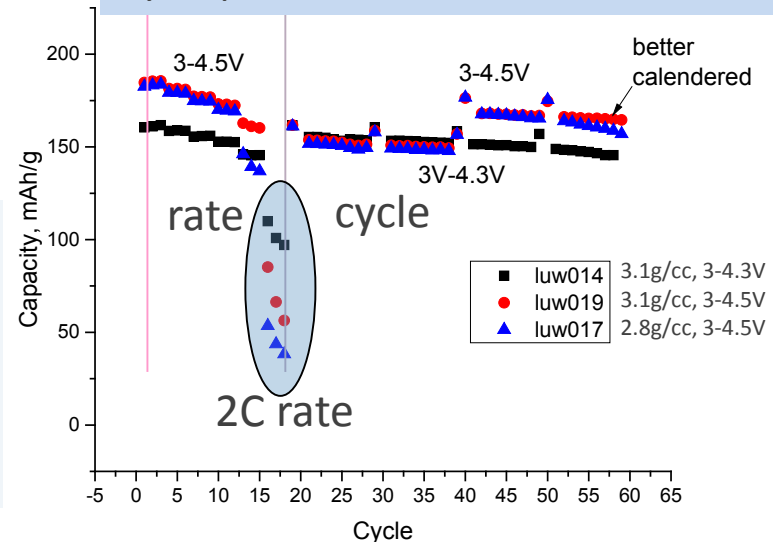
Physical Sciences Inc. has developed a rapid, low temperature coating approach that allows for much higher active material fractions to be achieved without a loss in performance, which will allow energy density increase using current commercially available materials.



EIS of Li/NCM523 electrode



Cycle performance of Li/NCM523 cell



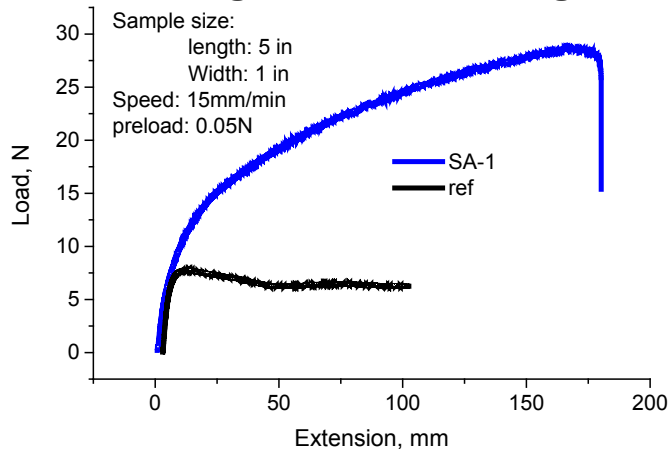
- Impedance measurement indicates that less interfacial impedance was also obtained for further calendered electrode from the smaller semi-arcs in both high and low frequency region.
- In addition, we noticed that further calendering can improve the electrode integrity.
- Similar capacity fading rate was observed for all electrodes regardless of electrode density and voltage window.

Ceramic coated separators

Ceramic coated Poly Ethylene (PE) membrane

- ❖ Isotropic property
- ❖ Thin film
- ❖ Thermal stability

Strong mechanical strength

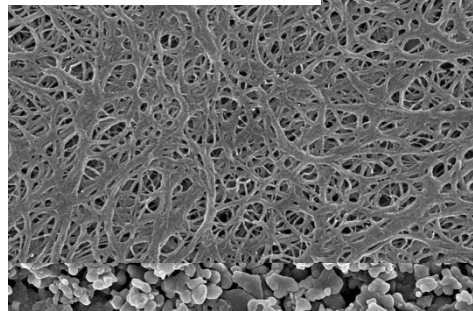


ShuangAo, Shanghai

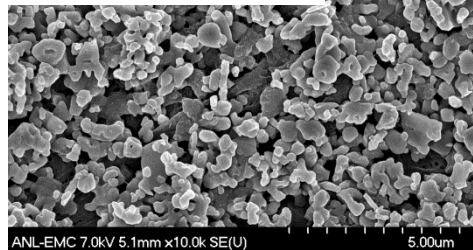
PE membrane: 12μm

Ceramic coated PE: 16μm

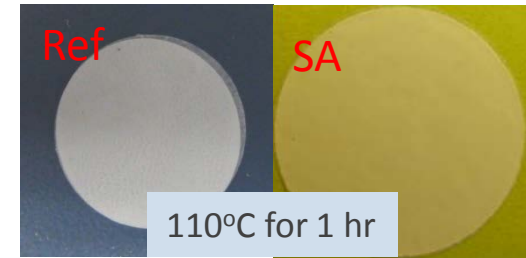
PE base separator



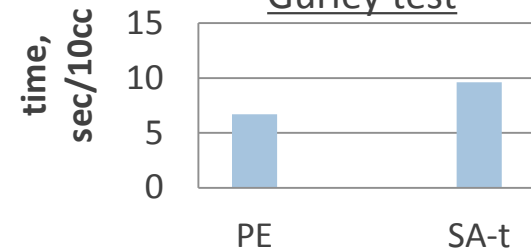
Ceramic coated PE



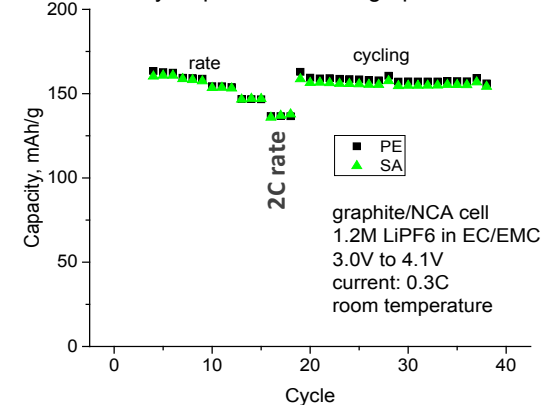
Good thermal stability



Gurley test



Cycle performance of graphite/NCA cell



- Equivalent electrochemical performance, in terms of rate and cycle life, was obtained for Graphite/NCA cell with ceramic coated separator.
- Less shrinkage for ceramic coated separator indicates the better thermal stability, which is critical for LIB in EV application.

Future Plan

- Continue to search and evaluate high energy density cathode and anode materials, such as silicon/silicon composite, nickel rich lithium metal oxides, et. al. as they become available.
- Surface modification and electrolyte effects on electrochemical and thermal stability of high energy electrode materials will be investigated.
- Various electrode materials and cell chemistries will be evaluated under cell fabrication facility to help to build the electrode library.
- Materials scaled-up by Material Engineering and Research Facility (MERF) will be validated.
- Continue to work closely with research institutes and industrial suppliers to enable the LIB technology for PHEV+EV applications.



Summary

- Silicon and its composite was investigated as anode materials for lithium ion batteries. Results include:
 - Good electrochemical performance and mechanical properties were obtained using a binder blend – PAA + SBR
 - FEC study suggested at least 10wt.% FEC is needed for Si electrode.
 - DSC results of Si electrode with FEC containing electrolyte is different to FEC free electrolyte.
- High energy cathode materials, nickel rich lithium transition metal oxides, were studied.
 - NCM523 with 4.5V cut-off voltage showed potential to be used for high energy applications.
 - Good electrochemical performance was obtained for the electrode with high fraction of PSI coated NCM523.
- Other cell components, such as redox shuttle, binder, separator, carbon additive have been studied and information was delivered to material supplier and internal facilities.
- Under CAMP Facility, several electrode library materials were collected and validated. Electrolyte and electrode materials from MERF were also validated.

Contributors and Acknowledgments

ANL

- Abraham, Daniel
- Burrell, Anthony
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